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### (54) WATER-BASED SURFACE-TREATING AGENT AND SURFACE-TREATED STEEL SHEET

#### (57)Abstract:

PROBLEM TO BE SOLVED: To obtain a chromium (VI)-free surface-treating agent which can give a treated sheet equivalent in performance to a chromate-treated one and to obtain a surface treated steel sheet on which a coating film of the surface treating agent has been formed.

SOLUTION: There is provided a water-based surface-treating agent containing (a) 50-97.9 wt.% (in terms of the solid matter) water-based resin, (b) 2-49.1 wt.% (in terms of the solid matter) colloidal silica, and (c) 0.1-10 wt.% (in terms of the solid matter) ammonium vanadate. It is desirable that the colloidal silica used is at least either of colloidal silica having adsorbed ammonium and colloidal silica coated with aluminum oxide.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the drainage system finishing agent and surface treated steel sheet excellent in corrosion resistance which are used for the object for household electric appliances, the object for building materials, and automobiles and which do not contain hexavalent chromium.

[0002]

[Description of the Prior Art] In the field of the surface treatment of a steel plate, the chromate treatment which contains hexavalent chromium for the corrosion-resistant improvement in a steel plate is used abundantly. However, it is known that this hexavalent chromium is tramp elements, and the demand to the finishing agent and surface treated steel sheet which do not contain this hexavalent chromium is increasing. Moreover, since the electrolysis clo mate whose chromium is a subject may also contain some hexavalent chromium, it may be hard coming to use it in the future. Although chromate treatment is used as surface treatment for primary rustproofing, such as a steel plate and a plating steel plate, paint, or covering, development of the processing technique which does not contain the chromium which replaces this chromate treatment is desired.

[0003] As a surface treatment technique which does not contain chromium, there is acid chloride processing in which phosphoric acid zinc processing etc. is not. however, chromium sealing is required, in order for phosphating to be inferior to a clo mate in corrosion resistance a little as primary rustproofing and to secure corrosion resistance also as paint surface treatment -- etc. -- as a clo mate's alternative technology, it is inadequate. In JP,5-195244,A "the metal finishing approach by the chromium free spreading mold acidity constituent" a) -- each of an anion component -- 1 -- with at least four fluorine atoms, 2 titanium, zirconiums and hafniums, a silicon, and at least one element chosen from the group which consists of boron Said anion component which contains the oxygen atom beyond 31 piece as an arbitration component, b) Cobalt, magnesium, manganese, zinc, nickel, tin, a zirconium, The cation component this whose cation total it is the cation component of the element chosen from the group which consists of iron, aluminum, and copper, and is 1/3 or more [ of the anion total of Component a ], c) The free acid of sufficient amount to maintain pH of said constituent within the limits of about 0.5 thru/or 5.0, the chromium by the aquosity acidity liquefied constituent which contains the constituent which forms an organic resin thin film by d direct drying as an arbitration component -- free -- formation -- the metal finishing approach which forms a coat in a surface of metal is proposed.

[0004] moreover, to "the constituent for metal finishing and art" of JP,7-145486,A a) A fluorine atom, and titanium, a zirconium, a hafnium, silicon and one or more sorts of atoms of boron, The component which consists of an anion containing an ionization nature hydrogen atom and/or one or more oxygen atoms, However, the number ratio of anions of the number of cations / component a of Component b = 1/5 or more c) The component which consists of a \*\*\*\* content organic oxy-anion and/or a phosphonic acid anion, d) -- the component which consists of one or more sorts of water solubility, a water-dispersion polymer, and polymer plasticity resin, and e -- the art which forms the enveloping layer

which does not contain chromium in a surface of metal with the aqueous constituent containing the acid component of the amount which is sufficient for keeping pH of this constituent at 5.0 from 0.5 is proposed.

[0005]

[Problem(s) to be Solved by the Invention] However, each metal finishing approach which does not contain the chromium proposed by the above-mentioned official report has come to fulfill corrosion resistance equivalent to the engine performance equivalent to the conventional thing by which chromate treatment was carried out, i.e., chromate treatment, and paint film adhesion. Made in order that this invention may solve the above-mentioned technical problem, the purpose is offering the finishing agent and surface treated steel sheet after treatment with the engine performance equivalent to the conventional chromate treatment, and for covering pretreatment.

[0006]

[Means for Solving the Problem] The place which this invention is made in view of said trouble, and is made into the summary (1) Colloidal silica by solid content conversion 50 to 97.9% of the weight by solid content conversion for drainage system resin 2 - 49.1 % of the weight, And the drainage system finishing agent characterized by containing an ammonium vanadate 0.1 to 10% of the weight by solid content conversion, (2) A drainage system finishing agent given in the above (1) characterized by being at least one kind in the colloidal silica by which colloidal silica was covered with the colloidal silica or the aluminum oxide to which ammonium was made to stick, [0007] In drainage system resin, in soluble in water (3) Or the above (1) characterized by containing the cross linking agent which can be distributed or a drainage system finishing agent given in (2), (4) Meltable [ in water ] or the cross linking agent which can be distributed is melamine resin. A drainage system finishing agent given in either of the above (1) characterized by containing this melamine resin 0.5 to 15% by solid content conversion to (3), (5) A drainage system finishing agent given in either of the above (1) with which drainage system resin is characterized by being at least one kind of emulsion in acrylic resin, urethane resin, and olefine resin to (4), [0008] (6) The surface treated steel sheet characterized by forming a coat on a steel plate using a drainage system finishing agent given in the above (1), (7) A surface treated steel sheet given in the above (6) characterized by being at least one kind of the colloidal silica by which colloidal silica was covered with the colloidal silica or the aluminum oxide to which ammonium was made to stick, (8) A surface treated steel sheet the above (6) characterized by meltable [ in water ] or containing the cross linking agent which can be distributed in drainage system resin, or given in (7), [0009] (9) Meltable [ in water ] or the cross linking agent which can be distributed is melamine resin. A surface treated steel sheet given in either of the above (6) characterized by containing this melamine resin 0.5 to 15% by solid content conversion to (8), (10) A surface treated steel sheet given in either of the above (6) with which drainage system resin is characterized by being at least one kind of emulsion in acrylic resin, urethane resin, and olefine resin to (9), (11) -- a surface treated steel sheet given in either of the above (6) characterized by a steel plate being a plating steel plate to (10) -- it comes out.

[0010]

[Embodiment of the Invention] The finishing agent and surface treated steel sheet of this invention are explained below. With drainage system resin, the resin of a distributed condition like water soluble resin, an emulsion, or a suspension is included. As a class of resin, olefine resin, urethane resin, acrylic resin, polycarbonate resin, an epoxy resin, polyester resin, alkyd resin, phenol resin, the resin as other coatings for printing, etc. are mentioned, and one or more kinds of resin can be chosen from these. Moreover, these copolymerization resin and mixed resin can also be used. As for the content of resin, it is desirable that it is 50 - 97.9% by solid content weight, and a processing coat serves as hard and it is [ the part which received processing exfoliates or ] hard coming to form membranes it at less than 50%. If 97.9% is exceeded, since the amount of other components which contribute to corrosion resistance etc. will decrease, corrosion resistance runs short.

[0011] Cross linking agent resin can be included in drainage system resin. As a cross linking agent, it is possible in water to use the resin in which soluble or distribution is possible, and water-soluble amino resin, the blocked isocyanate compound (urethane resin), an epoxy resin, etc. are mentioned to it. If

water-soluble amino resin (melamine resin, glycoluril resin, urea-resin) is used especially, the reinforcement of a coat becomes high, corrosion resistance will improve and a coat will become strong to a blemish. Although the addition is arbitrary since a cross linking agent changes in the optimal addition with the classes, in the case of water-soluble melamine resin, 0.5 - 15% is desirable as solid content weight in a processing agent. If less than 0.5% does not cover the expenses of reinforcement and 15% is exceeded, a coat will become hard too much, it will become easy to produce the crack of a part and exfoliation which were processed, and corrosion resistance will fall.

[0012] If at least one kind of emulsion in acrylic resin, urethane resin, and olefine resin is used as drainage system resin, especially corrosion resistance will improve. As colloidal silica, there are few impurities, such as sodium, and especially if it is a weak alkaline thing, it will not be limited. For example, "the Snow tex N", the "Snow tex NS", the "Snow tex NXS", the "Snow tex 30", the "Snow tex 40", the "Snow tex C", the "Snow tex S", "Snow tex 20L", the "Snow tex XS", the "Snow tex XL" (above, Nissan Chemical Industries, Ltd. make), "ADERAITO AT-20N", "ADERAITOAT-20A" (above, Asahi Denka Kogyo K.K. make), etc. be mentioned The addition of colloidal silica is 2 - 49.1% as solid content weight in a processing agent. At less than 2%, corrosion resistance falls and film strengths also run short. If 49.1% is exceeded, it becomes hard too much, and the crack of a processing coat, exfoliation, etc. will occur in the processing section, and corrosion resistance will worsen.

[0013] As colloidal silica, if at least one sort of an ammonium ion adsorption mold or an aluminum-oxide covering form is used, especially corrosion resistance will improve. In the above-mentioned example, "the Snow tex N", the "Snow tex NS", the "Snow tex NXS", and "ADERAITO AT-20N" is [ the former "ADERAITOAT-20A" ] the latter examples. The rust-proofing effectiveness of an ammonium vanadate is high. It is blended 0.1 to 10% by solid content weight conversion during a processing bath. At less than 0.1%, corrosion resistance runs short, and when 10% is exceeded, economical efficiency is missing.

[0014] The description of this finishing agent is that it used together van gin acid ammonium and colloidal silica. It sticks to van gin acid ammonium on the surface of colloidal silica, and it is thought that the rust-proofing effectiveness improves in multiplication. Especially, in the case of an ammonium in adsorption mold or an aluminum-oxide covering form, colloidal silica tends to adsorb, and is considered that corrosion resistance also improves.

[0015] Although especially pH of a processing bath is not necessarily limited, it is desirable that it is 8-10. A bath life becomes [ pH ] short less than by eight. When pH10 is exceeded, the dissolution of a base arises by alkalinity, a base metal is eluted during a processing bath, and there is a possibility of causing adhesion and a corrosion resistance fall. Moreover, bath stability may also fall. Since pH of a bath is adjusted, it is possible to add drugs.

[0016] Film formation nature is raised, and in order to form a uniform and smooth paint film, a well-known solvent, a film formation assistant, etc. may be added to the finishing agent of this invention. For example, the thing of an alcoholic system, a ketone system, an ester system, and an ether system can be raised. It is helpful also for preventing that water volatilizes at a stretch at 100 degrees C, and preventing generating of a support at the time of printing, to add a solvent.

[0017] Other components may be blended with the finishing agent of this invention. For example, they are a pigment, a surfactant, an additive, a silane coupling agent, etc. As a pigment, inorganic pigments, such as titanium oxide, a zinc oxide, a zirconium dioxide, a calcium carbonate, a barium sulfate, oxidization aluminum, kaolin gray, carbon black, and ferrous oxide, and organic pigments, such as cyanine blue, are illustrated. As a silane coupling agent, gamma-aminopropyl trimethoxysilane, gamma-aminopropyl triethoxysilane, gamma-glycidoxypopyltrimetoxysilane, gamma-methacryloxypopyl triethoxysilane, N-(2-(vinyl benzyl amino) ethyl)-3-aminopropyl trimethoxysilane, etc. are mentioned, for example. As an example of an additive, a defoaming agent, a leveling agent, a surface tension regulator, etc. are mentioned.

[0018] An above-mentioned finishing agent is applied on a steel plate by the well-known approach, and a surface treatment coat is formed by being dried and burned. Although especially the approach of spreading is not limited but a well-known approach can be used, the approach of a roll coat, blasting, an

air knife, a spin coat, a curtain coat, a dip painting cloth, etc. is mentioned, for example. After pretreating by the well-known approach on the surface of a steel plate if needed, the finishing agent of this invention can be applied. For example, they are rinsing, hot water rinsing, alkaline degreasing, acid washing, grinding, brushing, solvent degreasing, etc.

[0019] As a steel plate processed, cold rolled sheet steel, hot rolled sheet steel, a galvanized steel sheet, and an alloy element nickel, Cr, the zinc alloy plating steel plate which consists of any one or more kinds in Fe, Based on an above-mentioned galvanization or an above-mentioned zinc alloy plating steel plate, SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, and BaCrO<sub>4</sub> etc. -- the zinc system distribution plating steel plate which carries out the distributed deposit of the metallic oxide -- A hot-dip zinc-coated carbon steel sheet, an alloying hot-dip zinc-coated carbon steel sheet, a zinc-aluminum containing alloy plating steel plate, a chrome plating steel plate, a nickel-plating steel plate, a tinning steel plate, a stainless steel plate, etc. are mentioned.

[0020] Especially the coating weight after desiccation of a finishing agent is 0.2 - 10 g/m<sup>2</sup> preferably to 0.1 - 20 g/m<sup>2</sup> and a pan, although not limited. It is desirable. 0.1 g/m<sup>2</sup> Corrosion resistance cannot be secured in the following but it is 20 g/m<sup>2</sup>. If it exceeds, the drying time will become long and it will be hard to carry out efficient production. Moreover, the coat adhesion of the Erichsen processing section and the paint film adhesion of the Erichsen processing section after painting a finishing paint film fall. Furthermore, the corrosion resistance of the Erichsen processing section may fall. Although desiccation of a finishing agent and especially the conditions of printing are not limited, it is desirable for attainment board temperature to be 40-250 degrees C. At less than 40 degrees C, desiccation takes time amount, and it is not rational as industrial production. Moreover, it is not needed [ of capacity / high ], and desirable to exceed 250 degrees C, either. Moreover, hardening of a coat may become superfluous, a coat may become hard, and workability and processing section corrosion resistance may fall. Although the approach of desiccation is not limited, either, well-known approaches, such as hot blast heating, induction heating, near infrared ray heating, far infrared heating, and indirect heating, are applicable. The approach of carrying out the preheating of the steel plate, applying at the time of heat, and drying by remaining heat may be used.

[0021] It is a finishing agent by this invention, and it is also possible to process the same front face many times. That is, after forming the coat of the 1st layer on a steel plate by the above-mentioned approach, it is also possible to form a multilayer coat, as it says that a two-layer eye is formed by the still more nearly same approach. In this case, the coating weight after desiccation is 20 g/m<sup>2</sup>. It does not interfere, even if it exceeds. formation of each class -- since -- also \*\*\*\*(ing) -- it is not necessary to carry out on the same conditions

[0022]

[Example] This invention is explained with an example. Plating coating weight is 20g per one side/m<sup>2</sup>. The indirect desulfurization fat of the electrolytic zinc-coated carbon steel sheet which is 0.8mm of board thickness was carried out for 60-degree-C 10 seconds with 2% weight concentration solution of surfboard KURINA 155 (Nippon Paint Co., Ltd. make), and it dried after rinsing. Subsequently, the finishing agent of the presentation shown in Table 1 and 2 was applied by the roll coater, and it dried at the hot-air-drying furnace. Desiccation conditions were shown all over Table 1 and 2. In addition, amino alcohol 2 M-ABS (DMEA) (domestic chemistry company make) was used if needed for pH adjustment of a processing agent. Moreover, plating coating weight is 60 g/m<sup>2</sup> per one side. The hot-dip zinc-coated carbon steel sheet and plating coating weight which are 0.8mm of board thickness are 40 g/m<sup>2</sup> per one side. The alloying hot-dip zinc-coated carbon steel sheet and plating coating weight which are 0.8mm of board thickness are 20 g/m<sup>2</sup> per one side. The same approach also created and estimated the surface treated steel sheet which used as the negative the zinc-nickel alloy plating steel plate (11 % of the weight of nickel contents) which is 0.8mm of board thickness. The plating class was displayed all over Table 1 and 2. For EG, an electrolytic zinc-coated carbon steel sheet and GI are [ an alloying hot-dip zinc-coated carbon steel sheet and ZN of a hot-dip zinc-coated carbon steel sheet and GA ] zinc-nickel alloy plating steel plates. The contents of the finishing agent shown all over Table 1 and 2 are as follows.

[0023]

[Table 1]

表 1

No	樹脂等の種類	処置材料組成			メッキ皮膜		評価結果										備考												
		シリカ	メラミン	シリカ	Va濃度(%)	種類	付着量g/m <sup>2</sup>	板温℃	外観		密着性		上塗り密着性(2)		上塗り密着性(3)			耐腐蝕性	耐溶剤性	SST2hrs	SST24hrs		Gr**						
									平面	エリクセン	平面	エリクセン	平面	エリクセン	平面	エリクセン					平面	エリクセン		エタノール	灯油				
1	なし	ST-N	67	0	28	5	BC	0.1	120	5	10	10	10	10	10	10	10	5	1	5	4.5	20	70	赤錆	赤錆	無し	皮膜の付着量が少ないので耐食性が若干劣る		
2	なし	ST-N	67	0	28	5	BC	0.2	120	5	10	10	10	10	10	10	10	5	1	5	4.5	5	10	赤錆	赤錆	無し			
3	なし	ST-N	67	0	28	5	BC	0.3	120	5	10	10	10	10	10	10	10	5	2	5	4.5	2	5	85	赤錆	赤錆	無し		
4	なし	ST-N	67	0	28	5	BC	0.5	120	5	10	10	10	10	10	10	10	5	3	5	4.5	0	2	70	85	赤錆	赤錆		
5	なし	ST-N	67	0	28	5	BC	1	120	5	10	10	10	10	10	10	10	5	4	5	4.5	0	0	10	65	赤錆	赤錆	無し	
6	なし	ST-N	67	0	28	5	BC	5	120	5	10	10	10	10	10	10	10	5	4	5	4.5	0	0	1	2	赤錆	赤錆	無し	付着量が多く外観と上塗り密着性のエリクセン加工が密着性不良
7	なし	ST-N	67	0	28	5	BC	10	120	4	10	8	10	8	10	8	5	4	5	4.5	0	2	0	8	赤錆	赤錆	無し		
8	なし	ST-N	67	0	28	5	BC	15	120	4	10	8	10	8	10	8	5	4	5	4.5	0	25	0	70	赤錆	赤錆	無し		
9	なし	AT-20M	67	0	28	5	BC	1	120	5	10	10	10	10	10	10	5	4	5	4.5	0	0	5	30	赤錆	赤錆	無し		
10	なし	AT-20A	67	0	28	5	BC	1	120	5	10	10	10	10	10	10	5	4	5	4.5	0	0	5	40	赤錆	赤錆	無し		
11	S327	ST-N	59	8	28	5	BC	1	150	5	10	10	10	10	10	10	5	4	5	5	0	0	5	60	赤錆	赤錆	無し	実測値を加えると耐溶剤性、耐食性が向上 (Gr21と比較)	
12	S327	ST-N	51	16	28	5	BC	1	150	5	10	6	4	4	4	2	5	4	5	5	0	25	2	85	赤錆	赤錆	無し	実測値が多すぎエリクセン密着性、密着性、上塗り密着不良	
13	なし	ST-N	67	0	28	5	BC	1	50	5	10	10	10	8	10	8	5	4	5	4	0	0	15	80	赤錆	赤錆	無し		
14	なし	ST-N	67	0	28	5	BC	1	80	5	10	10	10	10	10	10	5	4	5	4.5	0	0	10	85	赤錆	赤錆	無し		
15	なし	ST-N	67	0	28	5	BC	1	150	5	10	10	10	10	10	10	5	4	5	4.5	0	0	7	60	赤錆	赤錆	無し		
16	なし	ST-N	67	0	28	5	BC	1	200	5	10	10	10	10	10	10	5	4	5	4.5	0	0	5	40	赤錆	赤錆	無し		
17	なし	ST-N	67	0	28	5	BC	1	220	5	10	10	10	10	10	10	5	4	5	4.5	0	0	5	40	赤錆	赤錆	無し		
18	なし	ST-N	65	0	0	5	BC	1	120	5	8	10	10	10	10	10	5	4	5	4	7	15	赤錆	赤錆	赤錆	赤錆	無し	シリカ添加なしで耐食性、密着性、耐溶剤性が劣る	
19	なし	ST-N	63	0	2	5	BC	1	120	5	10	10	10	10	10	10	5	4	5	4.5	0	2	70	85	赤錆	赤錆	無し		
20	なし	ST-N	80	0	15	5	BC	1	120	5	10	10	10	10	10	10	5	4	5	4.5	0	0	15	75	赤錆	赤錆	無し		
21	なし	ST-N	50	0	40	5	BC	1	120	5	10	10	10	10	10	10	5	4	5	4.5	0	0	10	65	赤錆	赤錆	無し	樹脂量で外観、密着性、上塗り密着性不良、耐食性もやや悪	
22	なし	ST-N	45	0	50	5	BC	1	120	4	10	8	10	6	8	6	5	4	5	4.5	2	25	70	赤錆	赤錆	赤錆	赤錆	無し	樹脂量で外観、密着性、上塗り密着性不良、耐食性もやや悪
23	なし	ST-N	80	0	60	5	BC	1	120	3	6	4	10	2	8	2	5	4	5	4.5	5	60	赤錆	赤錆	赤錆	赤錆	無し	樹脂量でシリカ多で外観、密着性、上塗り密着不良、耐食性も悪	
24	なし	ST-N	67	0	28	0	BC	1	120	5	4	2	4	2	2	2	5	4	5	4.5	85	100	赤錆	赤錆	赤錆	赤錆	無し	バナジン酸アンモニウム無添加で、密着性と耐食性悪い	

(注) 1) バナジン酸アンモニウム、2) 上塗り密着後の密着性試験、3) 上塗り密着後の密着性試験、4) SST7: サイマル327

[0024]

[Table 2]

2 碎

No	樹脂等の種類		処理剤組成		メッキ皮膜		評価結果										コメント				
	種類	製造会社	シリカ	メラミン	Va酸 <sup>1)</sup>	厚	付着量 <sup>2)</sup> g/m <sup>2</sup>	乾燥温度 <sup>3)</sup> ℃	外観	密着性 <sup>4)</sup> 平面	エリックセン	上塗密着 <sup>5)</sup> 平面	エリックセン	上塗密着 <sup>6)</sup> 平面	エリックセン	耐腐蝕性 <sup>7)</sup> 耐塩酸性		耐溶剤性 <sup>8)</sup> エタノール 灯油	SST24hrs <sup>9)</sup> 平面	Erickセン	Cr <sup>++</sup> <sup>10)</sup> 有無
25	なし	ST-N	67	0	28	0.1	BC	1	120	5	10	10	10	10	10	5	4	5	30	75	無し
26	なし	ST-N	67	0	28	1	BC	1	120	5	10	10	10	10	10	5	4	5	30	70	無し
27	なし	ST-N	67	0	28	3	BC	1	120	5	10	10	10	10	10	5	4	5	16	70	無し
28	なし	ST-N	67	0	28	10	BC	1	120	5	10	10	10	10	10	5	4	5	5	65	無し
29	なし	ST-N	67	0	28	15	BC	1	120	3	8	4	6	6	2	5	4	5	30	85	無し
30	なし	なし	100	0	0	0	BC	1	120	5	4	2	4	2	2	5	4	5	100	赤錆	無し
31	なし	ST-N	67	0	28	5	BC	1	120	5	10	10	10	10	10	5	4	5	5	15	無し
32	なし	ST-N	67	0	28	5	BC	1	120	5	10	10	10	10	10	5	4	5	10	70	無し
33	なし	ST-N	67	0	28	5	BC	1	120	5	10	10	10	10	10	5	4	5	5	15	無し
34	なし	ST-N	67	0	28	5	BC	1	120	5	10	10	10	10	10	5	4	5	25	80	無し
35	なし	ST-N	67	0	28	5	BC	1	120	5	10	10	10	10	10	5	4	5	25	85	無し
36	なし	ST-N	61	6	28	5	BC	1	150	5	10	10	10	10	10	5	4	5	3	10	無し
37	なし	ST-N	61	6	28	5	BC	1	150	5	10	10	10	10	10	5	4	5	10	65	無し
38	なし	ST-N	61	6	28	5	BC	1	150	5	10	10	10	10	10	5	4	5	4	12	無し
39	なし	ST-N	61	6	28	5	BC	1	150	5	10	10	10	10	10	5	4	5	20	25	無し
40	なし	ST-N	61	6	28	5	BC	1	150	5	10	10	10	10	10	5	4	5	20	75	無し
41	なし	ST-N	67	0	28	5	BC	1	120	5	10	10	10	10	10	5	4	5	20	75	無し
42	なし	ST-N	67	0	28	5	BC	1	150	4	10	10	10	10	8	6	2	4	35	90	有り
43	なし	ST-N	67	0	28	5	BC	0.2	60	4	10	8	6	6	6	1	2	5	10	75	有り
44	なし	ST-N	67	0	28	5	GI	1	120	5	10	10	10	10	10	5	4	5	5	65	無し
45	なし	ST-N	67	0	28	5	GA	1	120	5	10	10	10	10	10	5	4	5	4	45	無し
46	なし	ST-N	67	0	28	5	ZN	1	120	5	10	10	10	10	10	5	4	5	5	40	無し

注1) バナジウム酸アンモニウム、2) 上塗り塗装後の密着性試験、3) 上塗り塗装後、沸騰水30分浸漬し2.4時間放置後の密着性試験、4) SST27: サイマル327

注2) \*1: オレフィン/ウレタン=1/1

[0025] 1. Resin Class Olefin System: -- "-- High-tech S-7024" (Toho Chemical Co., Ltd. Make)  
Urethane system : "BONTAITA HUX-320" (the Asahi electrification company make)  
Acrylic : "AP-1058(12)" (Toagosei make)  
Epoxy system : "polysol 8500" (Showa High Polymer Co., Ltd. make)  
Polyester system : "PESUREJIN A-124G" (the Takamatsu fats-and-oils company make)  
[0026] 2. Cross Linking Agent S327 : Cymel 327 (Product made from Mitsui SAITEKKU)



3. Colloidal Silica ST-N: "Snow Tex N" (Nissan Chemical Industries, Ltd. Make)

AT-20N : "ADERAITO AT-20N" (Asahi Denka Kogyo K.K. make)

AT-20A : "ADERAITO AT-20A" (Asahi Denka Kogyo K.K. make)

ST-S: "the Snow tex S" (Nissan Chemical Industries, Ltd. make)

4. Ammonium vanadate : Wako Pure Chem industrial company make. Powder. It is used dissolving into a processing agent.

[0027] The following evaluations were performed about the created surface treated steel sheet.

1. The appearance of the processing film was judged by result appearance viewing, and the score was given. a score -- 5:homogeneity and 4:\*\*\*\* -- small -- those with nonuniformity, and 3: -- partial -- those with nonuniformity, and 2: -- on the whole, nonuniformity is severe those with nonuniformity, and all over 1:.

[0028] 2. Adhesion JIS of surface treatment coat K It judged by the squares tape method (clearance spacing of 1mm) of a publication to 8.5.2 of 5400. Moreover, it is JIS about a surface treated steel sheet. K It extruded 7mm with the Erichsen tester specified to 8.2 of 5400, tape exfoliation of the extruded part was carried out, and the adhesion of a coat was investigated. When it was hard to judge by viewing, the coat was dyed with 0.1% acetone solution of Methyl Violet, the coat existed in the dyed part, it presupposed that a coat does not exist in the part which is not dyed, and adhesion was judged. The same is said of evaluation of the appearance of the processing film.

[0029] 3. The ORUGA selection 100 (Nippon Paint Co., Ltd. make) which is a finishing paint film adhesion melamine alkyd paint was applied by the spray so that it might become 25 micrometers of desiccation thickness, and adhesion was checked by the same approach as two after desiccation printing with the air-heating furnace for 150-degree-C 20 minutes. Moreover, JIS K After extruding 7mm with the Erichsen tester of the convention to 8.2 of 5400, tape exfoliation of the Erichsen processing section was carried out by the same approach as 2, the adhesion of a paint film was investigated, and the score was given. a score -- 10; exfoliation nothing, 8; 5% or less of stripped plane product, and 6; 5% -- super- -- 10% or less of stripped plane product, and 4; 10% -- super- -- it considered as 30% or less of stripped plane product, and the stripped plane product of 2; 30% \*\*. Moreover, after being immersed in the boiling water for 30 minutes and leaving a surface treated steel sheet for 24 hours, the adhesion of the paint film of Ushiro who painted the Amylac paint film by the above-mentioned approach was investigated.

[0030] 4. The fingerprint was made to adhere to the coat of a fingerprint-proof nature surface treated steel sheet, the ease of being visible of a fingerprint was judged visually, and the score was given. 1 [ in which the remains of 2:fingerprint are conspicuous ] the score of the remains of 5:fingerprint is not visible to, the remains of a fingerprint seem whether to be 4:\*\*\*\*\*, whose remains of 3:fingerprint can be seen: It was presupposed that the remains of a fingerprint are very conspicuous.

[0031] 5. The waterdrop of dew condensation-proof nature distilled water was dropped at the coat side of a surface treated steel sheet, after leaving it on the 1st and drying water, the marks remainder was judged visually, and the score was given. 1 in which the remains remainder of 2: to which a score has those with marks remaining and the remains remainder of 3: in whether they are the remains [ of 5: ] remaining nothing ones and 4:\*\*\*\*\* is conspicuous: It was presupposed that the marks remainder is very conspicuous.

[0032] 6. Corrosion Resistance (SST)

It asked for the plate (it is a seal about the edge surface part and flesh-side surface part of a steel plate of as [ cutting ]), and the rate of generating area (%) of the white rust which performed the salt spray test (what is specified to JIS Z 2371) about the Erichsen 7mm processing section (it is a seal about the edge surface part and flesh-side surface part of a steel plate which were extruded 7mm with the Erichsen tester), and was generated visually.

[0033] 7. The solvent-resistance press oil was infiltrated into KAZE, it applied on the coat of a surface treated steel sheet, this oil was wiped off with the gauze into which ethanol or kerosene was infiltrated, the marks remainder of a coat was judged visually, and the score was given. In order to clean oil dirt etc., it is the trial for evaluating whether the activity wiped off with solvents, such as kerosene and

ethanol, may be done, and a coat receives damage with these solvents at this time. 1 in which the remains remainder of 2: to which a score has those with marks remaining and the remains remainder of 3: in whether they are the remains [ of 5: ] remaining nothing one and 4:\*\*\*\*\* is conspicuous: It was presupposed that the marks remainder is very conspicuous.

[0034] The evaluation result was shown in Table 1 and 2. The processing agent which added the silica (the Snow tex O, Nissan Chemical Industries, Ltd. make) to the chromic acid of 40% of rates of reduction so that it might be set to a chromic acid / silica = 1 / 3 (solid content weight ratio) is used for the compared inorganic chromate treatment, and it is coating weight as Cr with an air knife 50 mg/m<sup>2</sup> It adjusted and what was dried at 60 degrees C of desiccation board temperature was used (example No43 of a comparison). Moreover, the coating weight after desiccation is the processing agent which added the Snow tex N for strontium chromate to 67 % of the weight of olefin system resin 28% 5% as a rust-proofer by solid content conversion 1.0 g/m<sup>2</sup> The surface treated steel sheet which applied by the roll coater so that it might become, and was dried at 150 degrees C of attainment board temperature was also used as a comparison (example No42 of a comparison).

[0035] The rates of white rust generating area of salt fog 72-hour Ushiro of the surface treated steel sheet in which the coat which added the chromium system rust preventive pigment was formed into the chromate treatment steel plate of No43 considered as the comparison and the resin of No42 (flat-surface section) are 3% and 5%, respectively. The coat coating weight of the inside of an example and No1 is 0.1 g/m<sup>2</sup>. Except few levels, it has the corrosion resistance more than an EQC altogether, and it turns out that the finishing agent by this invention and a surface treated steel sheet are ingredients of high corrosion resistance which do not contain harmful hexavalent chromium. moreover, even after also boiling dew condensation-proof nature markedly, being excellent and setting it by the dew condensation environment, it turns out that there is no degradation by the defect of an appearance or the elution of a component.

[0036] For No8 of an example, adhesion of a coat is 15 g/m<sup>2</sup>. It has separated from the desirable range and is a little inferior to finishing adhesion (2nd order) and the corrosion resistance of the Erichsen section. No18 of the example of a comparison is a level without addition of a silica, and is inferior in corrosion resistance, adhesion, and solvent resistance. The examples No22 and No23 of a comparison have few resin contents, especially No23 of a silica addition is also superfluous, and an appearance, adhesion, finishing adhesion, and its corrosion resistance are bad. An ammonium vanadate is additive-free and the example No24 of a comparison has adhesion and bad corrosion resistance. The example No29 of a comparison has too many additions of an ammonium vanadate, and is bad. [ of adhesion and an appearance ] A silica and an ammonium vanadate are additive-free and the example of a comparison and No30 have adhesion and poor corrosion resistance.

[0037] When examples 5, 9, and No [ No41 and ] 10 are compared, it turns out that an ammonia adsorption mold (ST-N, AT-20N) and the aluminum-oxide covering form (AT-20A) has [ corrosion resistance ] a silica class better than other silicas (ST-S). The example of corrosion resistance which contains a cross linking agent as compared with No 15, 31, 32, 33, 34, and 35 which is the example which does not contain the cross linking agent which corresponds No 11, 36, 37, 38, 39, and 40 which is the example which contains a cross linking agent in drainage system resin, respectively is better, and it turns out that it excels also in solvent resistance.

[0038] When the class of resin is compared, it turns out that an olefin system, acrylic, and an urethane system are good. For example, it is good to compare No 5, 31, 32, 33, 34, and 35. In addition, the preservation stability of a processing agent shown in the example is good, and change of quality did not have at least 40 degrees C two weeks or more three months or more in ordinary temperature. Moreover, it checked that the engine performance as a surface treated steel sheet was also changeless at the passage of time by the storage for one year. According to this invention, also in the level which changed the plating class of negative, the surface treated steel sheet excellent in corrosion resistance, dew condensation-proof nature, and finishing paint film adhesion is obtained.

[0039]

[Effect of the Invention] As mentioned above, by combining the ammonium vanadate and silica which

do not contain hexavalent chromium in drainage system resin, compared with the conventional chromate treatment, the processing agent of chromium system rust preventive pigment content, or the processing coat, the finishing agent and surface treated steel sheet by this invention were excellent in dew condensation-proof nature, and are equipped with almost equivalent corrosion resistance. That is, the finishing agent which was excellent in low pollution at rust-proofing ability, and a surface treated steel sheet are offered.

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[Translation done.]